

Electrochemical copper (II) sensor based on chitosan covered gold nanoparticles

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Abstract This study outlines a new sensing platform based on glassy carbon electrodes modified by gold nanoparticles (AuNPs) for the determination of heavy metal. A glassy carbon electrode was modified by chitosan stabilized AuNPs. AuNPs were prepared by reducing gold salt with a polysaccharide chitosan. Here, chitosan acted as a reducing/stabilizing agent. The AuNPs were characterized with UV–Visible absorption spectroscopy, Fourier transform infrared spectroscopy, and transmission electron microscopy. Chitosan covered AuNPs were immobilized on the glassy carbon electrode for the determination of Cu (II) in aqueous solutions. The electrochemical determination of Cu (II) ions was performed using the differential pulse voltammetry technique. Some parameters for Cu (II) determination, such as pH, preconcentration time and electrolysis potential of Cu (II), were optimized. The detection limit was calculated as 5×10^{-9} mol L⁻¹ by means of the 3:1 current-to-noise ratio. The interference of Cr(III), Fe(II), Ni(II), Pb(II), Mg(II), Zn(II), Ba(II) ions was investigated and showed a

negligible effect on the electrode response. Recovery studies were carried out using tap water.

Keywords Gold nanoparticles · Chitosan · Heavy metal sensor · Cu (II) determination · Electrochemical sensor

1 Introduction

Environmental monitoring of heavy metal pollution in ecological samples is of great importance [1, 2]. The presence of heavy metals in streams, lakes, and ground water reservoirs causes several health problems [3]. One of the heavy metals is copper, and while a trace amount of it is important in biological systems, it can be toxic when taken in excess. Copper occurs in low concentrations in many real samples such as tap and wastewaters, food, drinks and soils. Rapid and accurate determination of copper in those samples is of great importance for timely assessment and effective prevention of its pollution [2]. Due to complicated interferents and low concentrations of copper, the determination methods require high sensitivity and good selectivity [4]. In recent years, various techniques have been reported for heavy metal detection, such as atomic absorption spectrophotometry (AAS) [4], atomic emission spectrophotometry (AES) [5], inductively coupled plasma spectrophotometry (ICP) [5], UV-spectrophotometry [6, 7], atomic fluorescence spectrophotometry (AFS) [8], and X-ray fluorescence [9]. However, these methods always need expensive apparatus and complicated sample preparation procedures [5]. In contrast, electroanalytical techniques are powerful tools for trace metal determination in the liquid phase [10]. These techniques have significant advantages, such as low cost, high sensitivity and are capable of simultaneously monitoring a variety of heavy metals [11]. Modification of the

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working electrode surface with a suitable reagent increases selectivity and sensitivity of analytical methods [12]. Modification can be performed using various methods, such as electrochemical, chemical, and physical. The modifiers used in these techniques include polymers [13], organic chelating groups [14] or nanoparticles [15]. It was reported that the gold nanoparticles (AuNPs) are useful for the development of modified electrodes [2]. They have been used for various purposes, such as the design and preparation of catalysts, development of catalytic activity or selectivity, good conductivity and for large surface areas [2, 16–18]. Various methods have been reported for the preparation of AuNPs [19]. Among these, one of the most popular is based on the reduction of chloroauric acid (HAuCl_4) using citrate to reduce (HAuCl_4) in water [20]. Also, recently the usage of polymers for synthesis of AuNPs has been reported. For example, AuNPs were prepared in the presence of chitosan [21, 22] and its derivative carboxymethylated chitosan [23]. Chitosan is a glycosaminoglycous obtained by heterogeneous deacetylation of chitin [24] and has a positive charge in solution. The amine chemical groups present in its structure means chitosan can chelate metal ions or biomolecules. Chitosan can also be used in the synthesis of AuNPs.

In this study, we synthesized AuNPs using chitosan that can act as both a protecting/reducing agent during AuNP synthesis and can chelate with metal ions [25]. To monitor the voltammetric behavior of Cu (II), a glassy carbon electrode was modified with chitosan/AuNPs (Ch/AuNPs-GC).

2 Experimental

2.1 Materials

Chitosan powder was obtained from Fluka AG (Buchs, Switzerland). $\text{Cu}(\text{NO}_3)_2$ was purchased from Merck AG (Darmstadt, Germany) and used as received. All other chemicals were of analytical grade and were purchased from Merck AG (Darmstadt, Germany). All solutions were prepared using deionized water, 18.2 M Ω cm free from organic matter, which was obtained from a Millipore purification system.

2.2 Instrumentation

Zeta potential measurements were made in a dynamic light-scattering apparatus (Zeta Sizer-Nano series Malvern Instruments) to examine the colloidal stability and charge of the AuNPs.

The morphology of the AuNPs was examined by TEM using a JEOL 2100 HRTEM (JEOL Ltd., Tokyo, Japan) transmission electron microscope.

UV–Visible absorption spectroscopy was used to monitor the plasmon absorption of the AuNPs produced, and spectra were collected using a Shimadzu UV-1800 UV–Vis spectrophotometer at wavelengths of 250–900 nm.

For FTIR analysis, the Au/Ch nanoparticles were centrifuged at 10,000 rpm and dried in eppendorf tube at room temperature. And, then the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrum of Ch/AuNPs was recorded in a Bruker Vortex 70 V FT-IR spectrophotometer within the range of 4000–400 cm^{-1} .

2.3 Preparation of chitosan/gold nanoparticles

Ch/AuNPs were prepared according to previously reported methods [26, 27]. Briefly, a solution of chitosan (1 % w/v) in 1 % acetic acid solution was prepared; due to poor solubility of chitosan the mixture was sonicated and kept overnight. 1 mL of 1×10^{-2} mol L^{-1} concentrated aqueous solution of HAuCl_4 , 2 mL of chitosan solution (1 % w/v), and 7 mL deionized water were mixed and heated to 90 °C in water bath for 10 min to yield a ruby-red solution.

2.4 Preparation of chitosan/gold nanoparticles-modified GC electrode (Ch/AuNPs-GC)

All steps represented in this section were performed before the usage of working electrodes in electrochemical experiments in order to avoid contamination by oxidation products and to obtain a clean renewed electrode surface. Before modification, the surface of the glassy carbon electrode was hand-polished with 1.0, 0.3, and 0.05 μm alumina–water slurries using a polishing cloth. Then, the electrode was washed and sonicated in pure water for 10 min to remove impurities. The polished and cleaned GC electrode surfaces were modified with Ch/AuNPs. In order to prepare Ch/AuNPs-modified GC electrode (Ch/AuNPs-GC), 5.0 μL solution of Ch/AuNPs was dropped on the electrode surface, and then it was dried at room temperature. Then, these modified electrodes were stored for 24 h over a 1 % solution of sodium tripolyphosphate (TPP) at +4 °C in a closed vessel. Prior to electrochemical measurements, the electrodes were thoroughly washed with distilled water to remove non-cross-linked TPP. This Ch/AuNPs-GC electrode was used for the Cu(II) determination by voltammetry technique.

2.5 Determination of Cu (II)

Electrochemical experiments were performed with a Gamry potentiostat (model Reference 600, USA) in a conventional three-electrode arrangement, equipped with a GC (3.0 mm diameter) working electrode, a platinum wire counter electrode and Ag/AgCl reference electrode. The

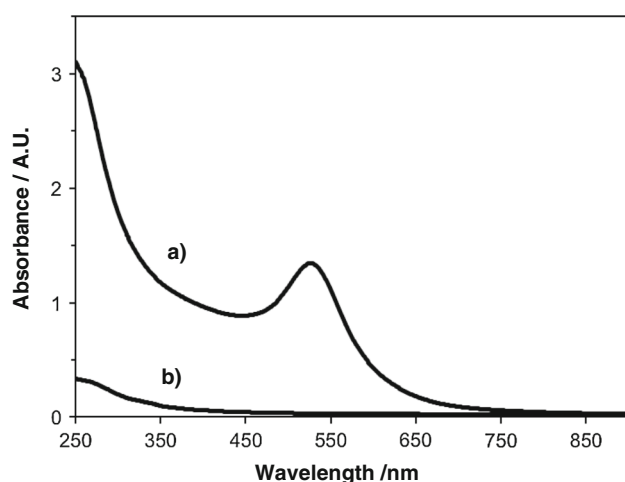


Fig. 1 UV–Vis absorption spectra of **a** Ch/AuNPs and **b** Ch

electrochemical Cu(II) determination step was performed using the differential pulse voltammetry (DPV) technique at room temperature. The procedure for the voltammetric determination of Cu (II) on a modified electrode included the following steps:

Accumulation step The modified electrode was immersed in a constantly stirred solution containing Cu (II) at given concentrations for 8 min.

Reduction step The modified electrode was washed and transferred into an electrochemical cell containing 0.05 mol L⁻¹ KNO₃ and then a electrolysis potential (−0.3 V) was applied for 150 s to reduce the presumably immobilized Cu(II).

Stripping step The potential was scanned from −0.7 to 0.6 V to strip the reduced Cu (II) in the DPV mode.

2.6 Analytical procedure

The Cu (II) determinations with Ch/AuNPs-GC electrode was evaluated by DPV, the parameters used for Cu(II) measurements were evaluated.

The reproducibility of analytical signals generated by differently modified GC electrodes during the determination of Cu(II) ions was evaluated three times by the detection of 1.0×10^{-4} mol L⁻¹ of Cu(II) ions.

The recovery studies were carried out by adding a solution that had a well-known concentration.

3 Results and discussion

3.1 Characterization of chitosan stabilized AuNPs

The optical absorption spectrum of AuNPs is a good indicator of their size and shape [28]. The UV–Vis absorption spectrum of the synthesized nanoparticles

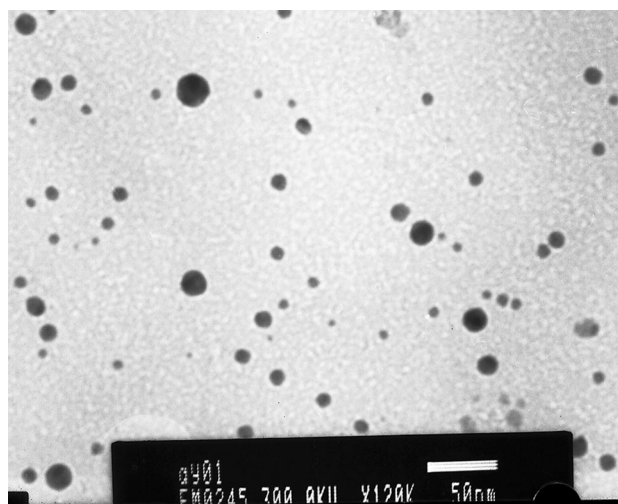


Fig. 2 TEM images of gold nanoparticles prepared by medium molecular weight chitosan

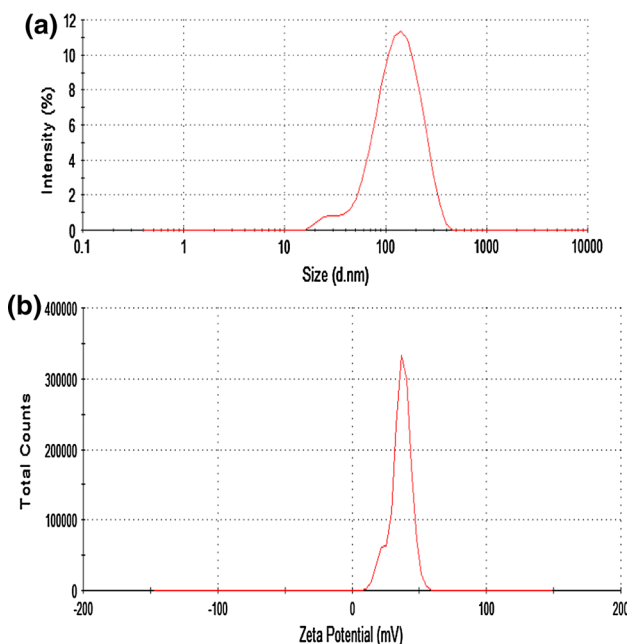


Fig. 3 **a** Size distribution and **b** zeta potential measurement of Ch/AuNPs

shows a sharp peak centered at 520 nm (Fig. 1a) that is a typical plasmon resonance band for AuNPs, suggesting the formation of AuNPs. This is the standard optical signature for the formation of gold nanospheres in solution. The AuNPs free chitosan solution has no absorption band in this range of wavelengths (Fig. 1b).

Chitosan, derived from chitin by partial deacetylation, is a polymer with poly-cationic properties in dilute acidic solutions. TEM analysis confirms no indication of the particle agglomeration was found, confirming that the

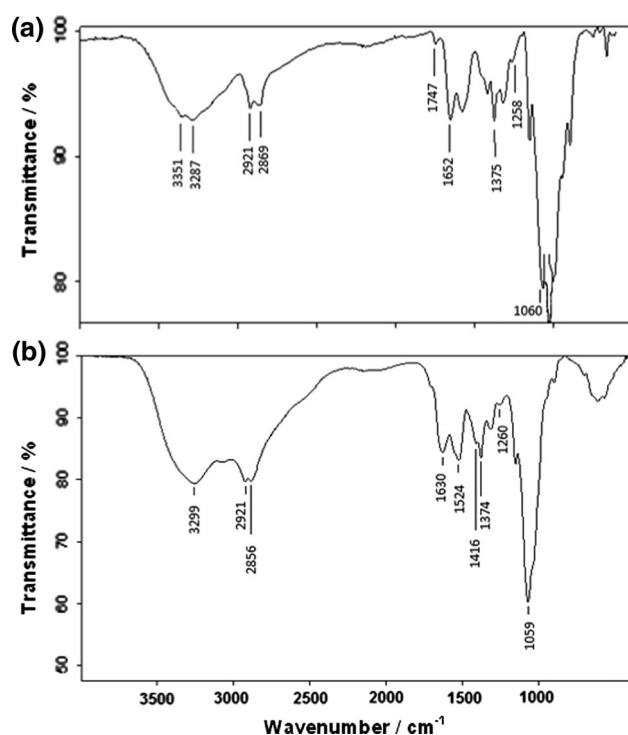


Fig. 4 FT-IR spectra of **a** Ch and **b** Ch/AuNPs

spectral features were caused due to chitosan capping of the AuNPs. TEM results showed that AuNPs had a spherical shape (Fig. 2).

The zeta potential value was positive 36.3 mV and this potential is a characteristic property of stable colloids [29]. It is well known that sodium borohydride reduced AuNPs are negatively charged [30]. Positively charged AuNPs indicated that the AuNPs were coated with cationic chitosan. The hydrodynamic diameter of chitosan reduced AuNPs was found to be 109 nm (Fig. 3).

The FT-IR spectra of the Ch and Ch/AuNPs in the range of 400–4000 cm^{-1} are shown in Fig. 4a and b, respectively. The characteristic IR absorption peaks of Ch were observed, which included a broad and strong band ranging from 3200 to 3400 cm^{-1} (stretching vibration of O–H and stretching vibration of N–H). The peaks located at 2921 and 2869 cm^{-1} can be assigned to asymmetric and symmetric $-\text{CH}_2$ groups, and the peak at 1652 cm^{-1} is characteristic of the C=O group of amides. The peaks at 1375 and 1258 represent C–N and C–O–C stretching, respectively. The peak at 1060 cm^{-1} is characteristic of C–O stretching vibration [31, 32]. However, the FT-IR spectra of Ch exhibited an additional band at 1747 cm^{-1} that resembled the presence of acetic acid [33] (Fig. 4a). It is worth noting that acetic acid was used to dissolve Ch in water so that it would remain within the Ch matrix after the preparation of the Ch/AuNPs process, in any stage of the process, it is somehow consumed.

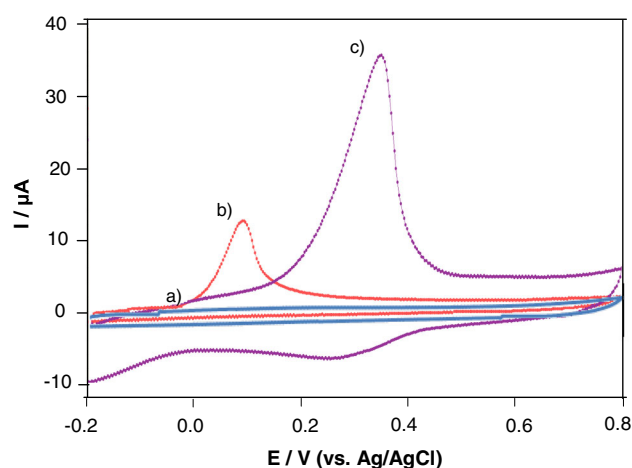


Fig. 5 Cyclic voltammograms of the **a** GC electrode, **b** Ch covered GC electrode, and **c** Ch/AuNPs covered GC electrode in the presence of $10^{-4} \text{ mol L}^{-1} \text{ Cu(II)}$

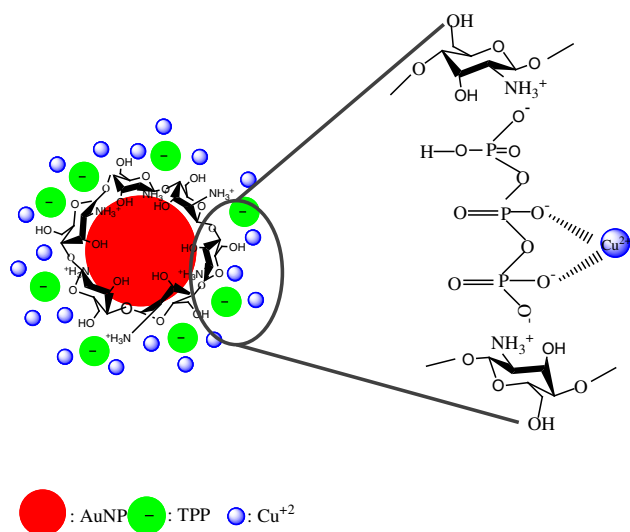
The FT-IR spectrum of Ch/AuNPs was rather similar to that of Ch (Fig. 4b). On the other hand, the twin peaks at 3351 and 3287 in the Ch spectrum disappeared in the Ch/AuNPs spectrum. Frequency shifting and disappearance of some peaks might be due to the interaction of the chitosan with the AuNPs. As reported in the literature, chitosan [$-\text{NH}_2$ and $-\text{CH}_2\text{OH}$] plays role as reducing agent for preparation metal nanoparticles but the reduction mechanism is not clear [34]. Hence, it was thought that this differences was due to effect of $-\text{NH}_2$ and $-\text{CH}_2\text{OH}$ groups in chitosan which can act as templates for nanoparticle growth.

3.2 Electrochemical determination of Cu(II)

The cyclic voltammograms of Cu (II) solution with bare and modified electrodes are shown in Fig. 5, and the peak potentials and peak currents of cyclic voltammograms were evaluated. The current of the peak obtained with the Ch modified electrode (Fig. 5b) and Ch/AuNPs-modified electrodes (Fig. 5c) is different from that obtained with the glassy carbon electrode (Fig. 5a).

Ch and Ch/AuNPs-modified electrodes showed sensitivity to Cu(II) ions; however, the Ch/AuNPs-modified electrode was more sensitive to Cu(II) ions at a broad concentration range, even at a low concentration level ($10^{-8} \text{ mol L}^{-1}$). For this reason, further experiments were performed using Ch/AuNPs-modified electrode. Ch/AuNPs-modified electrodes have higher active surface than bare Ch electrode due to AuNPs related to Ch (Scheme 1). Thus, sensitivity of the Ch/AuNPs to Cu(II) increased.

It is known that the environmental conditions are important parameters in the formation of metal ion based



Scheme 1 Schematic presentation of Cu(II) immobilized on the Ch/AuNPs

complexes. In order to investigate the analytical applicability of the Ch/AuNPs electrode for Cu(II) detection, the effect of various parameters such as pH, Cu(II) concentration, and incubation time were studied.

3.2.1 Electrolysis potential

The effect of electrolysis potential on peak currents of standard solution of Cu(II) was examined over the potential range of -0.1 to -0.5 V at an electrolysis time of 100 s. It was observed that the best current signal value was obtained at a deposition potential of -0.3 V (Fig. 6a). The effect of potential is almost the same between -0.3 and -0.4 V, so we selected -0.3 V for the electrolysis potential.

3.2.2 Effect of electrolysis time

The stripping peak current increased when the electrolysis time was increased up to 150 s. It then remained stable

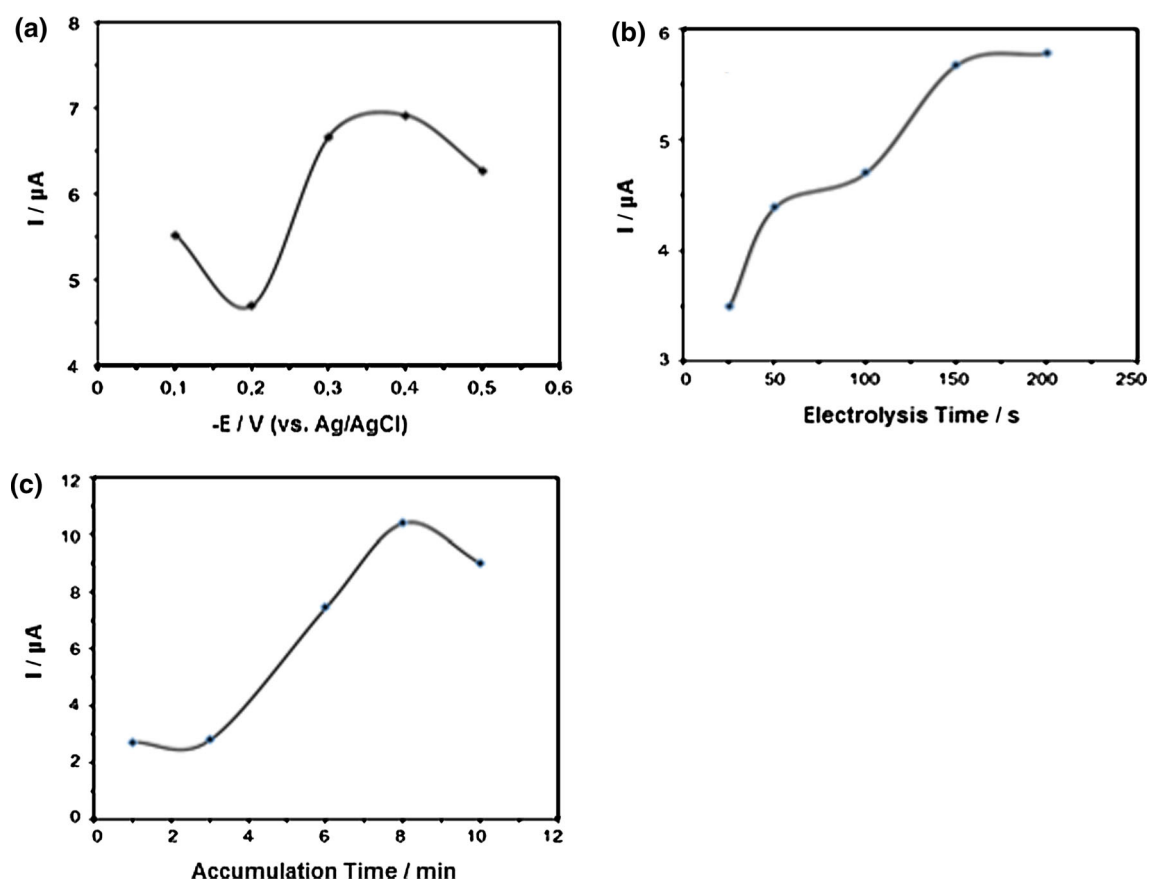


Fig. 6 Optimization studies for Cu(II) determination. **a** Effect of electrolysis potential, **b** effect of electrolysis time, and **c** effect of preconcentration time

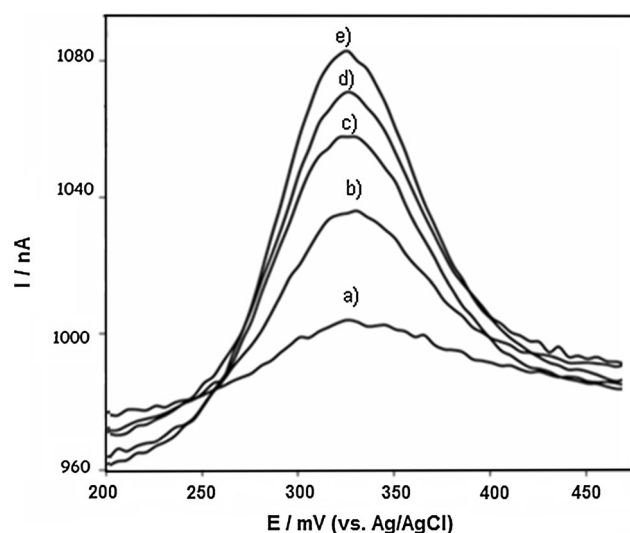


Fig. 7 Differential pulse voltammogram for **a** 1×10^{-8} , **b** 3×10^{-8} , **c** 1×10^{-7} , **d** 3×10^{-7} , and **e** 1×10^{-6} mol L $^{-1}$ Cu(II) concentrations. Step size: 5 mV, sample period: 0.5 s, pulse size: 25 mV, pulse time: 0.1 s

(Fig. 6b). This can be explained by the fact that the adsorption regions of Ch/AuNPs films on a GC electrode can be saturated. Therefore, 150 s was selected as the optimum electrolysis time.

3.2.3 Effect of pH

Chitosan has amine and OH groups and it is accepted that amine sites are the main reactive groups for metal ions. These reactive groups may interact with metal ions through different mechanisms, depending on the metal, the pH, and the matrix of the solution. The free electron doublet on nitrogen may bind metal cations at weak acidity pH [35–38]. The influence of pH on the accumulation of Cu (II) was examined in the pH range of 1.0–6.0, and the optimum pH was selected as 3 for Cu(II) determination (data not shown).

3.2.4 Effect of preconcentration time

To determine the most optimal preconcentration period, the Ch/AuNPs electrode was incubated in Cu(II) ion containing pH 3.0 for different periods between 2 and 10 min. It was observed that DPV signals increased up to 8 min and then decreased (Fig. 6c). This decrease may be due to the desorption of the partially adsorbed Cu(II) ions after 8 min.

As a result of these examinations, the most optimal conditions for the formation of Cu(II) complex on Ch/AuNPs electrode were found in pH 3.0 buffer solution, incubated for 8 min, and -0.3 V electrolysis potential.

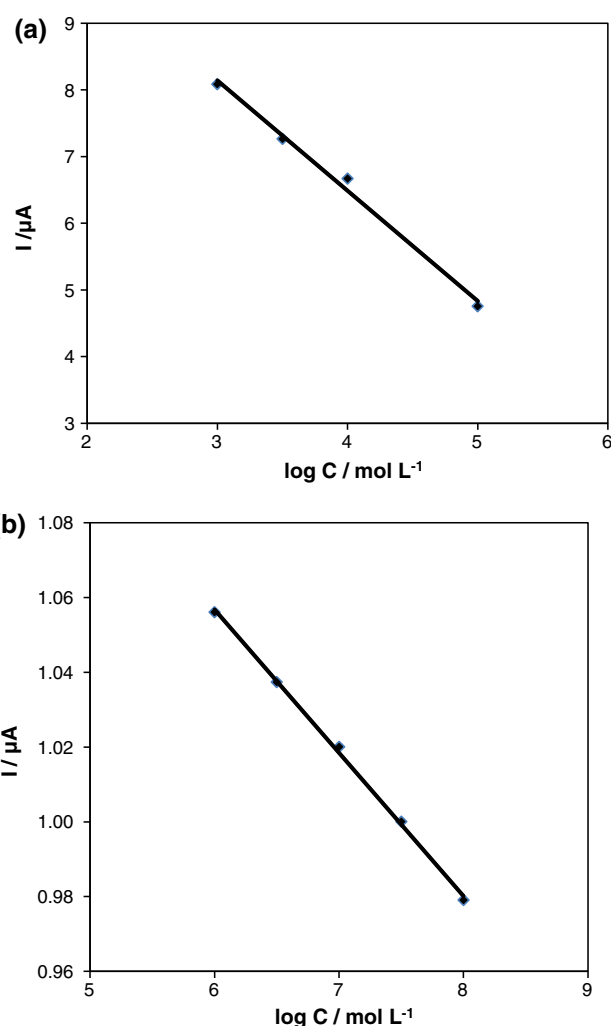


Fig. 8 Calibration curve of Cu(II) concentration between **a** 10^{-5} – 10^{-3} and **b** 10^{-8} – 10^{-6} mol L $^{-1}$

3.2.5 Calibration graph and reproducibility

The sensitivity of the Ch/AuNPs-modified electrode for Cu(II) ion was studied at different concentration values of Cu(II) ranging from 10^{-8} to 10^{-3} mol L $^{-1}$. The differential pulse voltammograms of Ch/AuNPs-modified electrode after incubation in solutions containing between 10^{-8} and 10^{-5} mol L $^{-1}$ Cu (II) ion concentration are presented in Fig. 7. The different peak currents registered by DPV technique increased with the increasing concentration of Cu(II) ions in aqueous solutions used for the treatment of the Ch/AuNPs-modified electrode.

The upper Cu(II) detection limit of the Ch/AuNPs-modified electrode was determined ranging from 10^{-5} to 10^{-3} mol L $^{-1}$ Cu(II) concentrations (Fig. 8a). A linear correlation between the peak current and Cu(II) concentration was found with a regression equation of $I(\mu\text{A}) = 1.665 \log[\text{Cu}^{2+}] + 13.162$ and a correlation

Table 1 Comparison of Ch/AuNPs sensor with other copper sensors

Modifier	Electrode	Method	Concentration (mol L ⁻¹)	LOD (mol L ⁻¹)	Accum. time	References
P4NA	GC	CV	0.5×10^{-8} – 0.5×10^{-12}	0.5×10^{-12}	–	[39]
Lc	MF	DPSA	1×10^{-5} – 1×10^{-9}	5×10^{-10}	4 min	[40]
–	Au	SASV	1×10^{-7} – 4×10^{-10}	2×10^{-10}	1.5 min	[41]
Polyphenol	GC	DPV	1.0×10^{-6} – 1.0×10^{-11}	1.0×10^{-11}	60 min	[42]
Polythiophene	Au/Al	SWV	1×10^{-5} – 1×10^{-7}	6×10^{-8}	5 min	[43]
AHMP	Au	CV	1×10^{-4} – 1×10^{-12}	8×10^{-11}	–	[44]
4-CP	SPE	SWV	1.8×10^{-7} – 7.5×10^{-9}	5×10^{-9}	10 min	[45]
Penicillamine	Au	CV	1×10^{-4} – 8×10^{-7}	4×10^{-7}	25 min	[46]
DMTD	Au	ASV	8×10^{-5} – 8×10^{-6}	4×10^{-7}	40 s	[47]
EDTA-CP	GC	SWV	1×10^{-7} – 5×10^{-10}	2×10^{-10}	10 min	[48]
NALc	Au	ASV	1×10^{-4} – 5×10^{-10}	1×10^{-10}	7 min	[49]
Ch/AuNPs	GC	DPV	1×10^{-3} – 1×10^{-8}	5×10^{-9}	8 min	This work

P4NA poly-4-nitroaniline, *AHMP* 4-amino-6-hydroxy-2-mercaptopyrimidine monohydrate, *4-CP* 4-carboxyphenyl, *DMTD* 2,5-dimercapto-1,3,4-thiadiazol, *EDTA-CP* EDTA bonded conducting polymer, *NALc* *N*-acetyl-L-cysteine, *Lc* L-cysteine, *GC* glassy carbon, *MF* mercury film, *SPE* screen-printed electrodes, *DPSA* derivative potentiometric stripping analysis, *SASV* subtractive anodic stripping voltammetry, *SWV* square wave voltammetry, *CV* cyclic voltammetry, *ASV* anodic stripping voltammetry

coefficient of $R^2 = 0.9927$. The lower Cu(II) detection limit of the Ch/AuNPs-modified electrode was determined within the range of 10^{-8} – 10^{-6} mol L⁻¹ Cu(II) concentrations (Fig. 8b). A linear correlation between the peak current and Cu(II) concentration was found with the regression equation of $I(\mu\text{A}) = 0.0384 \log[\text{Cu}^{2+}] + 1.286$ and a correlation coefficient of $R^2 = 0.9987$. The detection limit calculated on the basis of a signal-to-noise ratio of 3 was 5×10^{-9} mol L⁻¹.

3.2.6 Interference effect

The effects of Cr(III), Fe(II), Ni(II), Pb(II), Mg(II), Zn(II), Ba(II) ions on the stripping peak current of Cu(II) were investigated. To this aim, the differential pulse voltammogram of Cu(II) was compared with the voltammogram of interfering ions. In the voltammogram of Cr(III), Fe(II), Ni(II), Pb(II), Mg(II), Zn(II), Ba(II)) (each 1×10^{-5} mol L⁻¹) no additional peak related to interferents was observed (data not shown). This study showed that there is no interference effect of these ions for Cu(II) determination in working conditions.

3.2.7 Recovery

The determination of Cu(II) in spiked tap water samples was also carried out by the standard additions method at two different levels of concentration (1×10^{-5} and 3×10^{-6} mol L⁻¹). The mean recoveries for the two concentrations were 104 and 101 %, respectively. On the basis of these results, it may be affirmed that no influence of the matrix composition on the water sample was observed.

The reproducibility of the analytical signal is among the most important parameters of any analytical system. Therefore, the reproducibility of the Ch/AuNPs electrode was also investigated, and RSD was calculated as 9.4 %. The RSD values of both parameters were sufficient for this kind of sensor.

The electrochemical determination of Cu(II) has also been studied by other researchers. A number of different modified electrodes and different detection techniques were applied for this detection, as seen in Table 1. We believe that our modified electrode will be an alternative for Cu(II) determination with a short preconcentration time, low detection limit and easy preparation.

4 Conclusion

In this study, AuNPs were prepared by Ch which was used as both a reducing and stabilizing agent, and these nanoparticles were used for GC electrode modification. A modified GC electrode was used for Cu(II) determination and to the best of our knowledge, Cu(II) determination on the Ch covered AuNPs-modified GC electrode is reported for the first time. The results showed that AuNPs increased the Cu(II) sensitivity of Ch. The applicability of the AuNPs-modified GC electrode for the determination of Cu(II) ions with the LOD of 5×10^{-9} mol L⁻¹ was demonstrated in this study. The preconcentration time was selected as 8 min, which is a short time in comparison to other studies in the literature. We believe that AuNPs-modified GC electrodes could be very useful for the

determination of Cu(II) in industrial waste water and/or some other solutions containing Cu(II) ions.

Our next investigation related to the application of glassy carbon modified by chitosan covered AuNPs will be based on the application of these modified electrodes in the design of non-enzymatic glucose sensors.

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